

**METHODS OF FUNCTIONALIZING AND FUNCTIONALIZED  
METAL OXIDE PARTICLES AND MECHANICALLY STRONG AND  
TRANSPARENT OR TRANSLUCENT COMPOSITES MADE USING  
SUCH PARTICLES**

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The U. S. government has certain rights in this invention pursuant to grant number NIDCR 1 P01 DE11688.

**Field of the Invention**

10 The present invention relates to metal oxide particles comprising surface hydroxyl groups which are functionalized for a variety of reasons. The invention maximizes the fraction of hydroxyl groups functionalized by reacting the hydroxyl groups with two or more different functionalities comprising different steric hindrances. Some hydroxyl groups, called "reactive groups" are accessible to both functionalities. Hydroxyl groups that are not accessible to the functionalities having greater steric hindrance are accessible  
15 to functionalities with less steric hindrance. In a more preferred embodiment, the metal oxide particles are zirconium oxide particles, the mobile adhesion promoters are silanes, and the organofunctional coupling agents are zirconates. The composites primarily are suitable for dental and medical restoration; however, optical resins for use in high refractive index applications such as eyeglasses, resins for advanced prototyping, and  
20 adhesive applications also are possible.

**Background of the Invention**

Colloidal fumed silica nanoparticles currently are used as fillers in "microfilled" composite dental restorative resins. These particles can increase the hardness and wear resistance of photocured matrix polymers; however, the particles are not radiopaque and  
25 cannot be homogeneously dispersed within the matrix resin because of interparticle associations. The resulting coagulation leads to a substantial increase in viscosity and a

consequent decrease in composite workability. This places a severe limitation on the practical filler loading in "microfilled" composites.

The loading problem can be partially offset by incorporating prepolymerized organic fillers into the resin in which a relatively high level of colloidal silica is incorporated into highly crosslinked polymeric granules. The workability of the composite resins containing these fillers is maintained, and the cure shrinkage is somewhat reduced. However, the fillers also yield failure prone interfaces and cause a high degree of light scattering, thereby limiting the depth of cure.

Photocurable dental repair materials are needed which are transparent or translucent, radioopaque, have good workability, and have good mechanical strength and stability. The use of metal oxides as fillers in such materials results in transparent or translucent, radioopaque materials. However, the hydroxyl groups that tend to form at the surface of metal oxide particles in "protic" environments tend to make the surface of the particles hydrophilic. As a result, the metal oxide particles have difficulty being wetted or adhered to by relatively hydrophobic matrix monomers, such as acrylic monomers, which are non-polar or only weakly polar in nature.

Methods are needed to functionalize as many of these hydroxyl groups as possible in order to render the surface of metal oxide particles more hydrophobic.

### **Summary of the Invention**

The present invention provides functionalized metal oxide particles comprising a surface comprising a total quantity of hydroxyl groups comprising a complexed fraction and an uncomplexed fraction, the complexed fraction being effective to produce a coagulation point of about one minute or more after removal of a solvent from a mixture comprising said metal oxide particles and a matrix resin.

### **Detailed Description of the Invention**

The present invention relates to metal oxide particles comprising surface hydroxyl groups functionalized for a variety of reasons. Two primary reasons are (a) to render the surface polymerizable with a matrix resin, and (b) to render the surface hydrophobic. The present invention maximizes the "complexed fraction" of the total quantity of surface hydroxyl groups, or the fraction of the total quantity of surface hydroxyl groups that are functionalized. The present invention recognizes that the surface hydroxyl groups on metal oxide particles have different "accessibilities," and therefore have different reactivities towards groups with different steric hindrances.

For purposes of the present invention, functionalities with a "low steric hindrance" are defined as functionalities having a formula weight of less than about 250 grams/mole, preferably about 150 grams/mole or less. Functionalities with a "high steric hindrances" are defined as functionalities having a formula weight of about 250 grams/mole or more, preferably of about 300 g/mole or more.

Hydroxyl groups that are accessible to and complex with functionalities having a variety of both high steric hindrances and low steric hindrances are herein defined as "reactive groups." Hydroxyl groups that are accessible only to functionalities having low steric hindrance are herein defined as "less reactive groups."

Suitable agents with high steric hindrance include, but are not necessarily limited to organofunctional coupling agents, defined in more detail below. Suitable agents with less steric hindrance include, but are not necessarily limited to adhesion promoters, preferably mobile adhesion promoters, defined in more detail below. A preferred embodiment of the invention functionalizes the surface hydroxyl groups of metal oxide particles with a combination of both organofunctional coupling agents and adhesion

promoters. Using functionalities with differing steric hindrances maximizes the fraction of the total quantity of the surface hydroxyl groups functionalized, rendering the surface of the metal oxide particle less protic and more hydrophobic. In a preferred embodiment, substantially all of the hydroxyl groups are functionalized.

5 In a preferred embodiment, the metal oxide particles are zirconium oxide particles, the mobile adhesion promoters are silanes, and the organofunctional coupling agents are zirconates. The composites primarily are suitable for dental and medical restoration; however, optical resins for use in high refractive index applications such as eyeglasses, resins for advanced prototyping, and adhesive applications also are possible.

10 The invention encompasses the functionalized metal oxide particles alone, a mixture of the metal oxide particles combined with a resin comprising matrix monomers copolymerizable with functionalities on the metal oxide clusters, and the composite formed when the resin is copolymerized with the polymerizable functionalities on the surface of the metal oxide clusters. The mixture has good workability, and forms a  
15 composite which is mechanically strong and stable. Substantially any "metal" capable of forming an amphoteric metal oxide may be used to form the metal oxide particles. Suitable metallic elements include, but are not necessarily limited to niobium, indium, titanium, zinc, zirconium, tin, cerium, hafnium, tantalum, tungsten, and bismuth. Also suitable in place of the metal in the oxide is the semi-metallic compound, silicon. As  
20 used herein, unless otherwise indicated, the term "metal oxide" is defined to include silicon, and the word "metal," when used to refer to the metal oxide is intended to also refer to silicon.

The metal oxides may be made of a single metal, or may be a combination of metals, alone or combined with other impurities or "alloying" elements, including, but not

necessarily limited to aluminum, phosphorus, gallium, germanium, barium, strontium, yttrium, antimony, and cesium. Binary and tertiary compounds may be more easy to silanate, and may be produced by mixing precursors containing different metal or semi-metal groups. Preferred metal oxide particles comprise zirconium oxide. Alternately, it  
 5 may be preferable to use zirconium silicate particles (commonly known as "zircon"), as zircon is easier to silanate than zirconium.

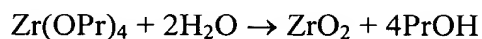
The metal oxide nanoparticles may be prepared using any known methods, such as "sol-gel" techniques, direct hydrolysis of metal alkoxides by water addition, forced hydrolysis of relatively low-cost metal salts, or non-hydrolytic reactions of metal  
 10 alkoxides with metal halide salts. Examples of such procedures are shown in the following references, each of which is incorporated herein by reference: W. Stöber and A. Fink, *J. of Colloid and Interface Science*, v. 26, 62-69 (1968); M.Z.-C. Hu, M.T. Harris, and C.H. Byers, *J. of Colloid and Interface Science*, v. 198, 87-99 (1988); M. Ocaña and E. Matijević, *J. of Materials Research*, v. 5(5), 1083-1091 (1990); L. Lerot, F.  
 15 LeGrand, P. de Bruycker, *J. of Materials Science*, v. 26, 2353-2358 (1991); H. Kumazawa, Y. Hori, and E. Sada, *The Chemical Eng'g. Journal*, v. 51, 129-133 (1993); S. K. Saha and P. Pramanik, *J. of Non-Crystalline Solids*, v. 159, 31-37 (1993); M. Andrianainarivelo, R. Corriu, D. Leclercq, P.H. Mutin, and A. Vioux, *J. of Materials Chemistry*, v. 6(10), 1665-1671 (1996); F. Garbassi, L. Balducci, R. Ungarelli, *J. of Non-*  
 20 *Crystalline Solids*, v. 223, 190-199 (1998); J. Spatz, S. Mössmer, M. Mo[umlaut]ller, M. Kocher, D. Neher, and G. Wegner, *Advanced Materials*, v. 10(6), 473-475 (1998); R. F. de Farias, and C. Airoidi, *J. of Colloid and Interface Science*, v. 220, 255-259 (1999); T. J. Trentler, T. E. Denler, J. F. Bertone, A. Agrawal, and V.L. Colvin, *J. of the Am. Chemical Soc.*, v. 121, 1613-1614 (1999); Z. Zhan and H.C. Zheng, *J. of Non-Crystalline*

Solids, v. 243, 26-38 (1999); M. Lade, H. Mays, J. Schmidt, R. Willumeit, and R. Schomäcker, Colloids and Surfaces A: Physiochemical and Eng'g Aspects, v. 163, 3-15 (2000); and the procedure described in "Sol-gel processing with inorganic metal salt precursors," authored by "Michael" Zhong Cheng Hu, licensable via Oak Ridge National Laboratory under ORNL control number ERID 0456.

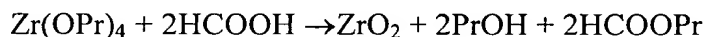
A preferred method of forming the metal oxide nanoparticles is water hydrolysis of corresponding metal alkoxides, preferably normal metal alkoxides having from about 1 to about 4 carbon atoms per hydrolyzable group. Where the metal used is zirconium, a preferred zirconium alkoxide for use in this procedure is zirconium propoxide. Although the following description is couched in terms of preparing zirconium oxide particles, the description applies equally to the preparation of other metal oxide nanoparticles.

If desired, the cluster synthesis may be enhanced using a suitable acid, preferably formic acid, as described in U.S. Patent No. 5,372,796 to Wellinghoff, incorporated herein by reference. Hydrolysis without using formic acid enhancement preferably takes place in the presence of excess alcohol as a diluent, preferably ethanol or propanol, most preferably n-propanol, in the presence of an inert gas, preferably nitrogen gas. Small droplets of water for hydrolyzing the zirconium alkoxide preferably are progressively added to the solution while stirring. The water droplets also preferably are diluted to a concentration of from about 1% (w/w) to about 3% (w/w) in a lower alcohol having from about 1 to about 3 carbon atoms, preferably propanol. In order to fully hydrolyze the zirconium alkoxide, the amount of water added must be twice the molar amount of the zirconium alkoxide unless the hydrolysis is enhanced using formic acid. During the addition of the water droplets, the solution is stirred vigorously. Typically, the addition of acid to produce a pH of about 3 is sufficient to form an adequate dispersion of zirconia

clusters. Substantially any acid having a pH of less than about 3 may be used for this purpose, suitable acids including but not necessarily limited to nitric acid, hydrochloric acid, sulfuric acid, and the like. The chemical stoichiometry is as follows:



5 In a preferred embodiment, a suitable organic acid is used to increase the rate of hydrolysis and to increase the amount of positive surface charge on the resulting zirconia clusters while producing only volatile byproducts. Any organic acid may be used as long as the ester resulting from the reaction has a low vapor pressure such that the ester will evaporate below about 200°C. In this embodiment, an amount of acid (preferably  
10 concentrated formic acid) which is about 1 to about 2 times the molar quantity of the alkoxide is added to the solution after adding the water/alcohol mixture. The solution is stirred for a prolonged period of from about 1 hour to about 24 hours, preferably about 12 hours. The reaction proceeds as follows:



15 When formic acid is used, the resulting clusters tend to grow large enough to scatter visible light, thereby giving the stirred solution a milky white appearance. If a smaller average cluster size is desired, then the system may be further acidified to a pH of near 1 by adding a strong acid, such as hydrochloric or nitric acid, in order to partially digest the clusters. The solution is stirred until achieving a desired average cluster size,  
20 preferably from about 20 nm to about 100 nm. The cluster size is measured using transmission electron microscopy (TEM), atomic force microscopy (AFM), or simple visual inspection based upon known light scattering phenomena.

Assuming perfect bonding between the particle and matrix, a decrease in particle size at a given volume fraction of particles will increase the elastic constraint on the

deforming matrix molecules and lead to an increase in modulus. However, as the particle size approaches molecular dimensions, the very closely spaced crosslinking points of high functionality within the matrix will substantially quench any large scale molecular motions. It is these motions which are important for energy dissipation and fracture toughness.

In order to accommodate both factors, the particles preferably are "nanoparticles," or particles having an average "diameter in nanometers" defined herein as from about 10 nm to about 150 nm, preferably about 50 to about 100 nm. The desired average diameter in nanometers is small enough to provide sufficient transparency for photopolymerization but large enough to provide effective fracture toughness after photopolymerization. In other words, the average diameter in nanometers permits the material to be effectively cured by photopolymerization and also provides effective fracture toughness after curing.

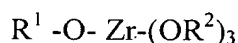
Once the desired average cluster size is achieved through adjustment of the solution pH, the clusters are organofunctionalized with an organofunctional coupling agent. Although irreversible binding is not an absolute necessity, the ideal organofunctional coupling agent readily and irreversibly condenses with reactive groups at the surface of the metal oxide clusters. The organofunctional coupling agent also provides a polymerizable functionality, preferably a double bond functionality, to the clusters to permit the clusters to copolymerize with a suitable surrounding organic matrix resin. The organofunctional coupling agents also preferably render the clusters more hydrophobic.

Suitable organofunctional coupling agents include polymerizable groups, including, but not necessarily limited to photopolymerizable groups such as vinyl, acryl, epoxy, or methacryl groups. Examples include, but are not necessarily limited to mono-,



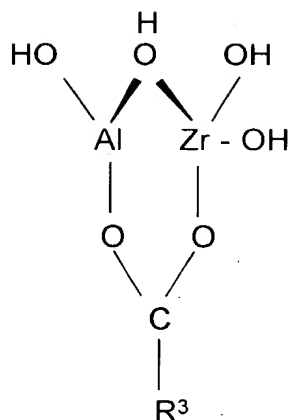
di-, and tri-functional silanes, isocyanates, zirconates, aluminozirconates, zirconyl methacrylate, titanates, and phosphonates. Preferred organofunctional groups, which increase the hydrophobicity of the clusters and also maximize the mechanical strength of the resulting composite are hydrolyzable zirconates having the following general

5 structure:



wherein  $R^1$  is selected from the group consisting of hydrolyzable alkyl groups and hydrolyzable alkenyl groups having 1 or more carbon atoms, said alkyl groups being effectively eliminatable from the system as free molecules either by volatilization or by  
 10 isolated copolymerization within the organic matrix resin, and  $R^2$  is selected from the group consisting of copolymerizable alkenyl substituents containing 2 or more carbon atoms.  $R^1$  generally may be eliminated by volatilization if the number of carbon atoms is less than 9. Preferred organofunctional groups are neopentyl (diallyl) oxy trimethacryl zirconates and neopentyl (diallyl) oxy triacryl zirconates (described in U.S. Patent No.  
 15 4,623,738, incorporated herein by reference).

Aluminozirconates having the following general structure also are preferred as organofunctional groups for zirconia clusters:



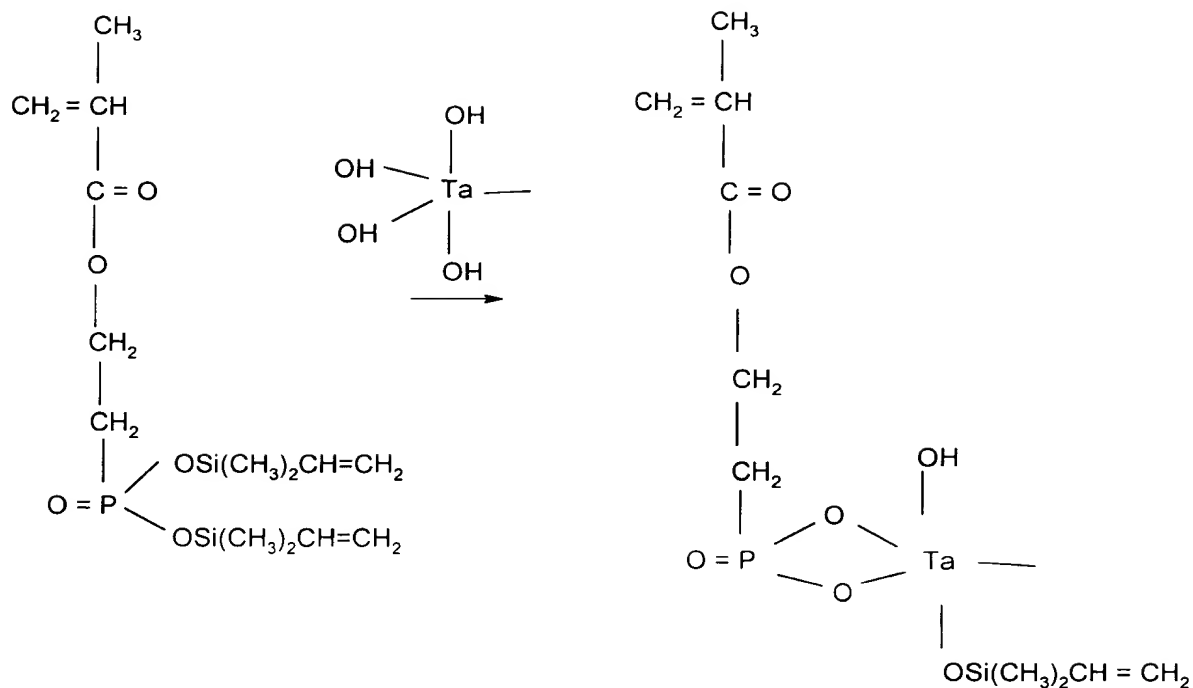
wherein  $R^3$  is selected from the group consisting of copolymerizable alkenyl groups and carboxyfunctional substituents containing 1 or more carbon atoms, respectively.

Preferred aluminozirconates are methacryloxy aluminozirconates (described in U.S.

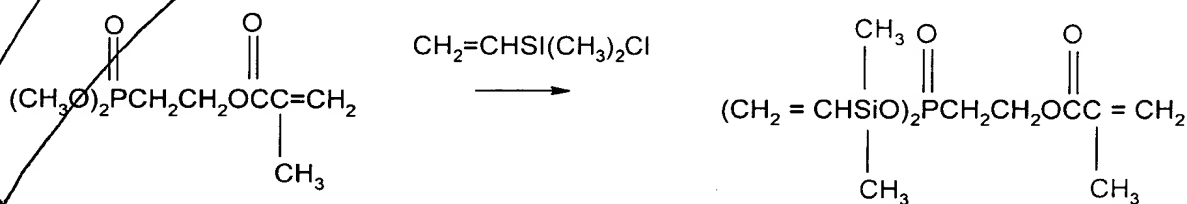
Patent Nos. 4,539,049 and 4,539,048, both of which are incorporated herein by

5 reference).

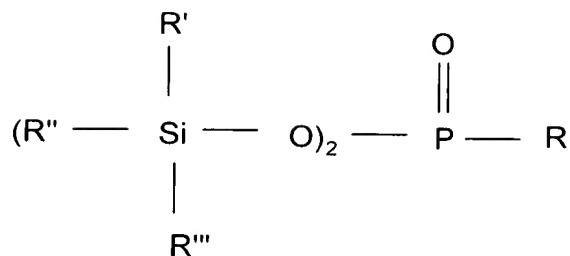
In another preferred embodiment, the polymerizable functionality is reacted with the oxide surface through a phosphonate linkage, which has good hydrolytic stability and will react with the metal-OH bonds only through the ester bonds, as shown below:



In order to make an especially active phosphonating species, the dimethyl ester of methacryl phosphonate was reacted with a silanating agent to form the hydrolytically unstable vinyl dimethyl silyl ester. The silanating agent can be a chloride, as shown below, or a bromide.



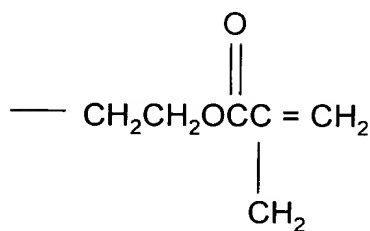
10 This reaction is quite generic and can be used to form any trialkylsilyl ester (e.g., trimethylsilyl) of any functionalized phosphonate, including vinyl phosphonate. Suitable esters have the general formula:



wherein R is a polymerizable group, such as a vinyl, acryl, or methacryl group, and R', R'', and R''' are the same or independently selected from the group consisting of alkyl groups and alkenyl groups.

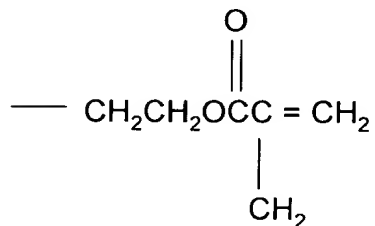
For example, in addition to the trialkyl silyl ester of vinyl phosphonate, phosphonates having the following groups can be used:

1. R is -CH=CH<sub>2</sub> and R', R'', and R''' each are -CH<sub>3</sub> groups;
2. R is



and R', R'', and R''' are each -CH<sub>3</sub>; and

3. R is



and R', R'' and R''' are each -CH<sub>3</sub>; and

R''' is CH<sub>2</sub>=CH<sub>2</sub>

5 The silyl phosphonate esters can serve two purposes. One purpose is as a surface phosphonating agent, and the other as a surface silanating agent which will generate the hydrophobic surface necessary for incorporation into hydrophobic monomers. If the silane is alkene functionalized, or otherwise functionalized with a polymerizable functionality, then the silane also acts as a coupling agent via the phosphonating agent.

10 The phosphonating agent may be incorporated into the metal oxide particles using any acceptable means. The phosphonating agent conveniently is incorporated by ester exchange of the metal ethoxide with an acid, such as formic acid. Alternately, the metal oxide prepared using conventional means may be exposed, preferably in an alcohol solution, to the silyl phosphonate and trifunctional silane. Any other suitable incorporation method is acceptable.

15 Even though a given metal oxide cluster may have experienced extensive phosphonating and silanating, the infrared spectrum still indicates the presence of a substantial amount of surface Ta-OH, the hydroxyls herein referred to as "less reactive groups." The remaining accessible Ta-OH may be further reduced by adding a trifunctional silane, such as 3-(trimethoxysilyl) propyl methacrylate to the formic acid mixture. This component also is useful since the multiple Ta-O-Si bonds formed by the

20 trifunctional silane are more hydrolytically stable than the monofunctional silanes. In addition, the silane effectively blocks access to unreacted Ta-OH bonds. Thus, interparticle hydrogen bonding associations between Ta-OH bonds on adjacent particles is blocked and premature phase separation of a tantalum rich phase in the hydrophobic matrix monomer is avoided.

The required amount of organofunctional coupling agent may vary from about 0.01 to about 0.3 times the molar content of the metal oxide, preferably zirconium oxide, in the ceramer. Quantities on the order of 0.2 times the molar content of zirconium oxide have been used to produce strong ceramers using dimethacrylate resins.

5           In order to organofunctionalize the clusters, the coupling agents are diluted with an excess of a suitable diluent, preferably an alcohol having from about 1 to about 4 carbon atoms, most preferably propanol, and added to the alcohol-zirconia-cluster solution. It is beneficial to maintain the acidity of the solution at a pH of from about 1 to about 3, preferably at about 3, in order for the reaction between the zirconia clusters and  
10       the primary coupling agent to be both timely and effective. The acidity may be maintained by adding a suitable inorganic acid, such as nitric acid. The resulting solution is agitated, preferably by stirring, for a prolonged period of time, preferably at room temperature or ambient temperature, in order to accomplish the organofunctionalization. A typical stirring time is about 3 days.

15           After the primary organofunctionalization has taken place, during which the "reactive groups" are functionalized, the zirconia clusters may be left in the alcohol solution for further treatment. Alternately, if the solids yield is to be assessed, the clusters may be dried by vacuum evaporation, weighed, and the clusters may be redissolved in one of the lower alcohols, preferably methanol, at a later time. In either case, it is  
20       preferable to also functionalize the less reactive groups by forming stable complexes or bonds between the less reactive groups and a secondary, highly mobile adhesion promoter in order to further compatibilize the metal oxide clusters with the relatively hydrophobic resin. The quantity of the "less reactive" hydroxyl groups complexed with the mobile adhesion promoter should be sufficient to displace as many hydroxyl groups from the

zirconia surfaces as possible and then to remain in place long enough to allow the particles to be homogeneously dispersed in a highly hydrophobic resin. This typically requires complexation or bonding with about 50% or more of the total quantity of hydroxyl groups.

5 Preferred "mobile adhesion promoters" are defined as surface-active molecules which strongly bind to the surface of the metal oxide cluster, preferably via primary chemical bonding, most preferably irreversibly. In a preferred embodiment, the polar end of the surface-active molecule preferably is bound to the surface by displacing the hydrogen of a hydroxyl group. The hydrophobic tail of the mobile adhesion promoter  
10 may intertwine with, but preferably does not chemically react with molecules in the matrix resin. Suitable mobile adhesion promoters include, but are not necessarily limited to silanes, phosphonates, phosphates, chelating agents, such as acetylacetone, fatty acids, such as stearic acid, fatty alcohols, and ester linked fatty acids. Preferred mobile adhesion promoters are silanating agents.

15 Preferred silanating agents are silanes bearing substituents selected from the group consisting of: from about 1 to about 3 alkyl groups having from about 1 to about 18 carbon atoms; from about 1 to about 3 alkenyl groups; and, from about 1 to about 3 substituents selected from the group consisting of chlorine, bromine, and an alkoxy group having from about 1 to about 4 carbon atoms. Preferred silanating agents have  
20 substituents selected from the group consisting of: one alkenyl group; two alkyl groups having from about 1 to about 3 carbon atoms; and, one alkoxy group having from about 1 to about 3 carbon atoms. A most preferred secondary surface agent is dimethyl ethoxy vinyl silane (DMEOVS) (U.S. Patent No. 4,504,231, incorporated herein by reference). DMEOVS has the benefit of increasing the double bond density of the cluster surfaces

while also being volatile enough that excessive amounts can be easily removed from the system. Nevertheless, the agent's greatest value is its ability to displace as many hydroxyl groups from the zirconia surfaces as possible and then to remain in place long enough to allow the particles to be homogeneously dispersed in a highly hydrophobic resin.

Any existing acid in the system will stabilize the silane against oligomerization and will catalyze its reaction with the cluster surfaces. Therefore, it is preferable to further acidify the solution to a pH of from about 1 to about 2, preferably to about 2, by adding a suitable inorganic acid, such as nitric acid. The resulting solution is again agitated, preferably by stirring at ambient conditions, for a prolonged period of time, typically from about 4 days to about 2 weeks.

Once the secondary coupling agent has been given sufficient time to react with the surface of the metal oxide, preferably at least 4 days, any acid (such as HCl) remaining in the solution may be removed by an acid scavenger. Any insoluble portion (generally less than 10% by weight) is removed by centrifugation, and any free protons in solution (i.e. HCl) is scavenged. Substantially any suitable acid scavenger may be used, such as polyamines and their copolymers. A preferred acid scavenger is polyvinyl pyridine. Using this acid scavenger, the system pH is adjusted upward to at least about 5, but not more than about 6. The supernatant solution is postreacted with a large excess of the secondary surface active agent in order to displace any hydroxyl groups remaining on the particle surfaces. If clouding of the solution occurs during postreaction, it may be desirable to centrifuge a second time and postreact again with an excess of the secondary surface active agent.



The functionalized nanoparticles then are ready to be mixed with the matrix monomers. Any transparent monomer comprising functional groups polymerizable with the coupling agent on the metal oxide clusters may be used. Suitable functional groups include, but are not necessarily limited to vinyl, acryl, epoxy, or methacryl groups. For dental applications, methacryl and acryl groups are preferred.

Generally, a solution of from about 10 wt% to about 30 wt% of zirconium oxide nanoparticles in lower alcohol, preferably methanol, is mixed with a solution of a suitable matrix monomers. It is possible that a higher wt% of zirconium oxide nanoparticles also may be used. Suitable matrix monomers include, but are not necessarily limited to glycerol monomethacrylate, glycerol dimethacrylate, hydroxyethylmethacrylate (HEMA), 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenylene]propane ("Bis-GMA), or ethoxylated bis-GMA and various blends of these monomers in combination with known viscosity reducers and photoinitiators or photoactivators. Known viscosity reducers include, but are not necessarily limited to triethyleneglycol dimethacrylate, and polypropylene oxide monomethacrylate. Known photoinitiators and photoactivators include, but are not necessarily limited to camphorquinone and 2-n-butoxyethyl-4-(dimethylamino)benzoate.

Since dimethacrylate resin monomers are soluble in the lower alcohols, it is convenient to add these resins directly to the existing zirconia solution, mixing them thoroughly. This liquid state mixing approach assures that all particles have sufficient opportunity to intimately adhere to the resin monomers. Once the mixture becomes homogeneous, the volatile agents may be directly removed by vacuum evaporation, yielding a single phase composite resin. Alternately, the resulting polymer may be isolated by filtration and/or centrifugation. If a the "complexed fraction" of the hydroxyl

groups at the surface of the zirconia clusters is sufficient, the zirconia clusters will not tend to interact with one another or agglomerate, even at near-neutral pH, once incorporated into a hydrophobic resin. Experimental samples contained 10, 20 and 30 wt% nanoparticle loadings.

5           The hydrophobicity of the nanoparticle can be increased by increasing the complexed fraction, or the number of functionalized Zr-OH bonds. The ability to alter the surface of the nanoparticle in a controlled manner permits control of the working time of the unpolymerized composite and modification of the cured microphase structure of the composite material.

10           For example, if a hydrophobic, matrix monomer and hydrophilic nanoparticles are dissolved in a common hydrophilic solvent, evaporation of the solvent will yield an initially mobile fluid which rapidly will phase separate to form an elastic gel. Elastic properties are generated by an interpenetrating network phase of hydrophilic metal oxide nanoparticles within the hydrophobic matrix.

15           If, on the other hand, the hydrophobic matrix monomer and the relatively hydrophobic nanoparticles are mixed in a common solvent and the solvent is evaporated, microphase separation will proceed more slowly providing increased working or storage time in the mobile state.

          Generally, the organofunctionalized nanoparticles suspended in an alcohol  
20   medium (an "alcosol") are co-dissolved with dental-grade acrylic monomers by addition directly to a flask containing the alcosol suspension. The organofunctionalized nanoparticles dissolve completely in the alcosol. The original alcohol is then evaporated away with the aid of a vacuum pump. The weight of the composite is measured

progressively. For a small batch (~5g), the total evaporation time is approximately 2 hours.

When the weight of the composite no longer changes with continued pumping, the solvent is considered to be sufficiently removed, and the composite is ready to be used, for dental restoration, for stereolithography, etc. In the lab, the composite is used to form specimens, *e.g.*, small molds, and the molds are centrifuged to remove any entrapped air.

Coagulation of the composite is a physically observable phenomenon. Initially upon removal of the solvent, the composite is a “flowable,” soft paste, which is easily worked with a spatula. Over time, the paste begins to stiffen. At a definite point in time, herein called the “coagulation point,” the material takes on a semi-solid, gelatinous form which is soft, but fractures under pressure. At the coagulation point, the composite no longer flows. If the nanoparticles are sufficiently functionalized, the coagulation point occurs upon the elapse of the following periods of time after removal of the solvent: about 1 minute or more; preferably about 1 hour or more; more preferably about 2 hours or more; and, most preferably about 4 hours or more.

With increased working time, the kinetic development of phase separation can be terminated at different stages by polymerization of the matrix monomer or prepolymer. Interconnectedness of the oxide network can have a strong influence on mechanical, permeability and electrical properties of the material.

By appropriate matching of the surface properties of the nanoparticles and the matrix monomer, it is possible to make a one phase system or generate a very fine phase separation that is insufficient to scatter light to a depth of at least about 1 millimeter, preferably to about 2 millimeters or more. This is of specific importance in many applications because several millimeters in thickness of such a material can be uniformly

photocured to a solid. In addition, opacifying particles can be added to the transparent base for control of cosmetic features.

The invention will be better understood with reference to the following examples, which are set forth for purposes of illustration only:

5                    Example 1.  $\text{ZrO}_2$  Cluster Synthesis by Aqueous Hydrolysis

A solution of 10.8367 g of 70% (w/w) zirconium propoxide in propanol was added to a round-bottom flask under nitrogen gas reflux to yield  $2.32 \times 10^{-2}$  moles of the pure alkoxide. The solution was diluted by further adding 60 ml normal propanol while  
10 stirring with a magnetic stir bar. To completely hydrolyze the alkoxide, the amount of water added was twice the molar amount of zirconium propoxide, i.e.  $4.63 \times 10^{-2}$  mole. 0.84 ml water was diluted with 40 ml normal propanol, and this solution was added to the flask dropwise (by burette) while stirring vigorously. The solution gradually became cloudy as the water was added. In order to increase the rate of hydrolysis, the solution  
15 was slightly acidified by adding 0.16 ml concentrated nitric acid to the flask. The solution clarified somewhat, remaining slightly hazy. Stirring was continued for about 2 hours. 2.3 ml ( $-4.63 \times 10^{-2}$  mol.) of pure neopentyl(diallyl) methacryl zirconate was diluted in 10 ml propanol and the resulting solution was added to the flask dropwise (by pipette), and the solution was stirred for 2 more hours. The system was then further  
20 acidified by adding 0.9 ml concentrated nitric acid, resulting in a system pH of about 3. Stirring was continued for about 3 days.

After stirring for 3 days, the flask was evacuated by pumping until only a dry powder remained. The powder was weighed and determined to have a mass near 6.3 g. The powder then was dissolved in methanol with the aid of a vortex mixer until the solids  
25 concentration was in the range of 10-20%(w/w). 15.3 ml ( $-9.26 \times 10^{-2}$  mol.) of pure

dimethyl ethoxy vinyl silane was added to the solution. To prevent polymerization of the silane over time, the solution was further acidified by adding 0.7 ml concentrated nitric acid, resulting in a system pH of about 2. Stirring was continued for one week, and the solution was then neutralized with about 5 g polyvinyl pyridine (2% crosslinked) such  
5 that the system pH was greater than 5 but no more than 6. The polymeric base was isolated by filtering the solution.

Once the powder has been solvated, cluster concentration is known and is assumed to remain constant during neutralization. This assumption has been confirmed by re-drying aliquots of the solution. Any and all dilutions preferably are recorded.

10 Example 2.  $\text{ZrO}_2$  Cluster Synthesis Enhanced by Formic Acid

10.3540 g of 70%(w/w) zirconium propoxide solution was added to a round-bottom flask under nitrogen gas reflux. The solution was diluted with 60 ml normal propanol while stirring with a magnetic stir bar. 0.4 ml water was diluted in 20 ml  
15 normal propanol, and this solution was added to the flask dropwise (by burette) while stirring vigorously. The solution became slightly cloudy after the water was added. Stirring was continued for approximately 12 hours, and 1.25 ml concentrated formic acid was added. The resulting solution was stirred for at least 30 minutes, and then 2 ml concentrated hydrochloric acid was added, reducing the system pH to nearly 1. Once the  
20 solution was clarified to the point of being only slightly hazy, 2.2 ml of pure neopentyl(diallyl) methacryl zirconate was diluted in 10ml propanol and added to the flask dropwise (by pipette). Stirring was continued for at least 2 hours, and the solution was pump vacuum dried to a powder.

The resulting powder was dissolved in methanol with the aid of a vortex mixer  
25 until the solids concentration was in the range of 10-20%(w/w). 14.6 ml of pure dimethyl

ethoxy vinyl silane was added to the solution and the solution was stirred for one week. 4-5 g polyvinyl pyridine (2% crosslinked) was added while monitoring the system pH until it was between 5 and 6. The polymeric base was isolated by centrifugation.

### Example 3. Composite Formation Using Zirconia Clusters

14.7783 g of a solution having a concentration of clusters of 10.15%(w/w) was added to a round-bottom flask, yielding 1.50 g clusters. Added to this solution, and mixed thoroughly, was 6.00 g of a blend of 37 wt% bis-GMA, 25 wt% tetra ethylene glycol dimethacrylate (TEGDMA), 37.5 wt% bis-EMA (an ethoxylated version of bis-GMA) with 0.2% camphorquinone and 0.3% 2-n-butoxyethyl-4-(dimethylamine)benzoate (CQ/amine) (photoinitiator for on-demand polymerization).

The flask was evacuated after mixing in order to remove the volatile methanol and silane from the system. The yield was 7.50 g of composite resin having a solids content of 20%(w/w). The mechanical properties ( $\pm 1$  standard deviation) of a variety of composite specimens prepared as indicated are given in the Table below:

The resin had a fluid consistency which was easily manually packed into transparent silicone molds in order to produce mechanical testing specimens for flexural and fracture toughness testing. Once filled, the specimen molds were centrifuged to aid in the removal of air bubbles prior to photocuring. Specimens were spot cured using a dental curing lamp ( $\lambda = 470$  nm, QHL 75, Dentsply) for a minimum of one minute at each location. The flexure specimens were 2.5 x 2.5 x 25 mm in size while the fracture toughness specimens were 8 mm square and less than 4 mm thick. The geometry and testing approach was taken from the ASTM E399 specification, although the specimen size is somewhat smaller than that recommended. The cured specimens were tested to failure, and the fracture surfaces were analyzed by optical microscopy.

Mechanical Property	Unfilled Model Resin	70% Silica-Filled Model Resin	20% Zirconia Filled Model Resin (Formic Acid Used)	20% Zirconia-Filled Model Resin (Inorganic Acid Used)
Breaking Stress (psi)	15271.66 ± 1,695.98	18658.58 ± 2,185.93	38522.47 ± 1,804.53	21816.34 ± 1,995.32
Flexural Modulus (GPa)	2.36 ± 0.21	7.87 ± 0.53	15.73 ± 1.93	12.80 ± 1.08
Fracture Toughness [ksi(in <sup>1/2</sup> )]	0.4557 ± 0.0436	0.3711 ± 0.2033	0.4586 ± 0.0979	--

Preliminary TEM images revealed that the average particle size was probably much smaller than the expected ~ 100 nm value, which was consistent with the high optical transparency of the sample. The average flexural strength of the resins was as much as 251.8 MPa. The elastic modulus of the materials was as much as 15.73 GPa. The fracture toughness did not deteriorate with filler loadings up to 30 wt%.

Many modifications and variations may be made to the embodiments described herein without departing from the spirit of the present invention. The embodiments described herein are illustrative only should not be construed as limiting the scope of the present invention.